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Kinetics of epoxidation of jatropha oil with peroxyacetic and peroxyformic acid catalysed by acidic ion exchange resin

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Abstract

The kinetics of epoxidation of jatropha oil by peroxyacetic/peroxyformic acid, formed *in situ* by the reaction of aqueous hydrogen peroxide and acetic/formic acid, in the presence of an acidic ion exchange resin as catalyst in or without toluene, was studied. The presence of an inert solvent in the reaction mixture appeared to stabilise the epoxidation product and minimise the side reaction such as the opening of the oxirane ring. The effect of several reaction parameters such as stirring speed, hydrogen peroxide-to-ethylenic unsaturation molar ratio, acetic/formic acid-to-ethylenic unsaturation molar ratio, temperature, and catalyst loading on the epoxidation rate as well as on the oxirane ring stability and iodine value of the epoxidised jatropha oil were examined. The multiphase process consists of a consecutive reaction, acidic ion exchange resin catalysed peroxyacid formation followed by epoxidation. The catalytic reaction of peroxyacetic/peroxyformic acid formation was found to be characterised by adsorption of only acetic (or formic) acid and peroxyacetic/peroxyformic acid on the active catalyst sites, and the irreversible surface reaction was the overall rate determining step. The proposed kinetic model takes into consideration two side reactions, namely, epoxy ring opening involving the formation of hydroxy acetate and hydroxyl groups and the reaction of the peroxyacid and epoxy group. The kinetic and adsorption constants of the rate equations were estimated by the best fit using nonlinear regression method. Good agreement between experimental and predicted data validated the proposed kinetic model. From the estimated kinetic constants, the apparent activation energy for epoxidation reaction was found to be 53.6 kJ/mol. This value compares well with those reported by other investigators for the same reaction over similar catalysts.

Keywords: In situ epoxidation; Jatropha oil; Acidic ion exchange resin; Peroxyacetic acid; Peroxyformic acid; Kinetics

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1. Introduction

The application of modified plant oils in chemical industry is becoming more and more interesting and desirable because of their availability from renewable resources. The unsaturation of the vegetable oils rich in oleic, linoleic and linolenic acyl groups may be used to introduce functional groups like epoxides. In particular, epoxidised fatty acid derivatives from vegetable sources can be used in various domains, for example, as stabilisers and plasticisers in polymers, as additives in lubricants, as components in plastics and in urethane foams and, in general, as intermediates for a large number of commodities (Gruber, 1993; Gan et al., 1995; Sherringham et al., 2000; Bunker and Wool, 2002; Petrovic et al., 2003). Several processes are available for the preparation of epoxidised oils. The most widely used process is the epoxidation of unsaturated compounds with either pre- or *in situ* formed organic peroxyacids. *In situ* epoxidation using hydrogen peroxide with either acetic or formic acid as the peroxygen carrier has achieved commercial importance (Latourette et al., 1960; Eckwertt et al., 1978; Hildon et al., 1979).

Although numerous references exist in the technical literature concerning the methods of epoxidation of different olefinic substrates, very few are concerned with systematic kinetic studies. Epoxidation can be carried out by different methods, depending on the feedstock, epoxidation reagent, catalyst, and solvent. Epoxidation of vegetable oils can be carried out in solution or in bulk, with *in situ* formed or preformed peroxyacids,

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with homogeneous or heterogeneous catalysts (Findley et al., 1945; Gall and Greenspan, 1955; Wisniak et al., 1964; Abraham and Benenati, 1972; Zaher et al., 1989; Yadav and Satoskar, 1997). The *in situ* process is a widely used method between these two, because when the organic peroxyacid is preformed, there are some safety issues as the concentrated peroxyacid is unstable and explosive. A kinetic model for *in situ* epoxidation of anchovy oil with partially preformed peroxyacetic acid in the presence of a resin catalyst has been reported (Wisniak and Navarrete, 1970). In the range of operating variables, the epoxidation and ring opening were described by a pseudo first order reaction, applying the principle of the stationary state.

The kinetics of *in situ* epoxidation of oleic acid with hydrogen peroxide and acetic acid, and that of methyl ester of palm olein by peroxyformic and peroxyacetic acid, both carried out in the presence of sulfuric acid as a catalyst, concluded that the rate determining step was the formation of peroxyacetic or peroxyformic acid (Chou and Change, 1986; Gan et al., 1992). Rangarajan et al. (1995) have reported the kinetic parameters for *in situ* epoxidation of soybean oil by peroxyacetic acid, in the presence of sulfuric acid as the catalyst, but they have treated it as a two-phase system. The proposed model also predicted the effect of the addition of an inert solvent on epoxidation. Musante et al. (2000) have employed a heterogeneous kinetic model that takes into account the physicochemical interaction of reactive species in a polar liquid phase with an ion exchange resin (acting both as selective sorbent and heterogeneous catalyst) to analyse the peroxyacetic acid synthesis from acetic acid and hydrogen peroxide in an aqueous solution. Activities rather than molar concentrations in the polymer phase and specific (dry weight of catalyst basis) rather than volume-based expressions were found to give the best constitutive equations for the heterogeneous reaction rate. However, it must be noted that Musante et al. (2000) have presented the modelling of only one of the sub-system, namely, the kinetics of formation of PA in the heterogeneous aqueous phase–polymer (acidic catalyst) phase system.

With an acidic ion exchange resin as the catalyst for the epoxidation of vegetable oils, the porous structure of the solid catalyst and the size of the natural unsaturated triglycerides were found to minimise the side reactions and thus improved selectivity (Kirk et al., 1965). The presence of an inert solvent in the reaction mixture appeared also to stabilise the epoxide product, and minimise the side reactions, such as the opening of the epoxy ring, especially at higher temperatures (Gan et al., 1992).

Since the acidic ion exchange resin has been reported to affect the selectivity, we thought it desirable to study the epoxidation of jatropha oil in bulk, with an objective of obtaining higher oxirane selectivity. Heterogeneous catalytic processes of this sort are characterised by three phases namely, (1) an acidic solid catalyst phase, whose behaviour is highly dependent on the physicochemical properties of the system, together with (2) an aqueous phase (acetic acid, hydrogen peroxide and water), immiscible with (3) the organic phase. The kinetics of such a system is very complex even for the first order reactions, and some assumption such as Langmuir–Hinshelwood–Hougen–Watson (L–H–H–W) type reaction mechanism may help to simplify the rate equations (Froment and Bishoff, 1990).

In this work we have studied the kinetics of epoxidation of jatropha oil in or without toluene with peroxyacetic and peroxyformic acid generated *in situ* from acetic/formic acid and hydrogen peroxide in the presence of an acidic ion exchange resin as a catalyst.

The main purpose of this study is to develop value-added products form locally available renewable resources in India (Openshaw, 2000; Srivastava and Prasad, 2000). The filtered fresh jatropha oil from properly stored seed is light yellow in color. The composition of the oil is similar to other oils, which are used for edible purposes, the presence of some antinutritional factors such as toxic phorbol esters renders this oil unsuitable for use in cooking (Gubitz et al., 1998). Thus, it is a good choice as the starting oil for production of epoxide. A further objective of this work was to propose a mathematical model for the reaction system and the estimation of the unknown kinetic parameters of the proposed model.

2. Materials and methods

2.1. Materials

Jatropha Curcas oil was obtained from Purandhar Agro & Biofuels (Pune, Maharashtra, India). Glacial acetic acid (AR Grade), Formic acid (95–97%), aqueous hydrogen peroxide (30 wt%), and iodine trichloride were procured from Merck India Limited (Mumbai, Maharashtra, India). The acidic ion exchange resin (Amberlite IR-120) was obtained from SISCO Research Laboratories (Mumbai, Maharashtra, India). HBr in acetic acid was obtained from SISCO Research Laboratories (Mumbai, Maharashtra, India) and then diluted with glacial acetic acid to prepare 0.1(N) HBr. All the other chemicals were obtained from reputed firms. They were used without further purification.

2.2. Experimental setup

The epoxidation reactions were carried out in a fully baffled mechanically agitated contactor made of glass, and having 6.5 cm i.d. and 250 mL capacity, equipped with a 2 cm-diameter six bladed glass turbine impeller, and a reflux condenser. The reactor assembly was immersed in a thermostatic water bath, whose temperature was maintained within ±1 K.

2.3. Experimental procedure

The epoxidation method as reported in our previous work was followed (Goud et al., 2006). The required amount of jatropha oil was placed in the reactor. Calculated amount of acetic/formic acid and the acidic ion exchange resin catalyst were added. The mixture of oil, acetic/formic acid, and the acidic ion exchange resin was stirred for about 30 min. Then calculated amount of